



CO oxidation on phosphate-supported Au catalysts: Effect of support reducibility on surface reactions

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ABSTRACT

Previous work has shown that Au supported on FePO₄ can be stable and active for CO oxidation and that oxygen from the FePO₄ can participate in the CO oxidation. In this paper, we have used gas transient DRIFTS-QMS, Raman, temperature-programmed reduction and CO oxidation activity measurements to compare adsorption and oxidation of CO on two comparably loaded Au catalysts supported on both a reducible phosphate support, FePO₄, and a non-reducible support, LaPO₄. H₂-TPR confirms that the Au/FePO₄ catalyst is highly reducible and that the reduction is strongly promoted by the Au, while neither LaPO₄ nor Au/LaPO₄ are reducible up to 500 °C. The nature of Au species was determined by CO adsorption. For Au/FePO₄, cationic Au is present after oxidative treatment, and metallic Au dominates after reductive treatment. The majority of the cationic Au observed on the FePO₄ support undergoes *in situ* reduction to metallic Au during rt CO adsorption. For Au/LaPO₄, no cationic Au is observed, but metallic Au is present after both oxidative and reductive treatment. In addition, metallic Au is accompanied by anionic Au, not seen on Au/FePO₄, which accumulates during CO exposure, even after an oxidative pretreatment. Unexpectedly, CO interacts rapidly with Au/LaPO₄ to evolve CO₂ and form both adsorbed CO₂ and “carbonate-like” species, even though the LaPO₄ is non-reducible and Raman fails to find evidence for loss of structural oxygen. H₂ coevolves with CO₂ during CO-TPR of Au/LaPO₄ (but not for Au/FePO₄) leading to the conclusion that surface hydroxyl is the source of oxygen during CO exposure to Au/LaPO₄. Anionic Au is associated with the vacancies remaining after reaction of hydroxyl with CO.

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1. Introduction

Gold is now well known to be an active catalysts for CO oxidation which it can do well and selectively in the presence of H₂ [1]. For this reason, it is of potential use in cleanup of CO present in air or in H₂ fuel streams in fuel cell applications [2]. Au is also able to oxidize CO using H₂O, i.e. to catalyze the water–gas shift (WGS) reaction, a capability which may ultimately lead to commercial application [3–5]. Other catalytic uses for selective oxidation have also been examined [6]. Although its activity for these reactions can be very high, its performance and stability depends sensitively upon preparation conditions and the support used, and for this reason, it has been the subject of considerable interest during the past decade. Much debated are the oxidation state of Au in its active state and the reaction pathways and intermediates in CO oxidation and WGS. It is widely held that the support plays a role in mitigating these pathways and in affecting the oxidation state of the Au.

An important question in understanding the pathways for CO reaction is how O₂ is activated. Previous work shows that low-index Au single crystal surfaces such as Au(111) do not readily

adsorb O₂ [7,8] or more accurately only weakly physisorb O₂ without dissociation. However, atomically or highly dispersed Au is apparently able to dissociate O₂, yielding adsorbed O atoms, suggesting that low-coordination Au sites are required [9]. Transient IR and isotope exchange experiments on catalysts containing highly dispersed Au clusters/nanoparticles on TiO₂ and Al₂O₃ have provided evidence that metallic Au clusters adsorb CO readily, but they do not adsorb much oxygen and the adsorbed oxygen is catalytically very active [10,11]. Experiments with isotopically labeled O₂ near room temperature (rt) indicate that reactant O₂ does not scramble, implying that all dissociated O₂ reacts rapidly with CO rather than to associatively recombine [12]. Theoretical analysis supported by DFT calculations [13,14] and analysis of experimental size-dependent measurements [15] suggest that low-coordination kink and edge sites are necessary for CO oxidation activity, presumably because these are the sites necessary for O₂ activation. Very specific structures of Au have been found experimentally that are highly active in CO oxidation [16], possibly for their ability to bind or activate O₂ [17]. Besides direct reaction between CO and dissociated O on Au particles, a second pathway that has been suggested for CO oxidation is through a CO–OH intermediate, referred to as carboxyl or hydroxycarbonyl. Carboxyl has been identified by DFT as a reactive intermediate, and the carboxyl-mediated route is

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suggested to be the dominant pathway for WGS on Cu surface [18]. Promotion of CO oxidation by H₂O or H₂ observed on Au catalysts has also been attributed to this carboxyl intermediate [10,19–21]. For Au on Al₂O₃ or TiO₂, promotion by H₂O cannot be attributed to WGS reaction [12] since WGS does not occur at the reaction temperature. Apparently, the H persists through many turnovers rather than react to evolve H₂. In these cases where hydroxyl is present either from adventitious water or from H₂ co-feed, this pathway may be an important contributor to CO conversion. Reaction by this mechanism may occur at a Au⁺ site or may involve hydroxyl on the support or at the Au support interface, suggesting a role of the support in promoting CO oxidation. Another pathway for CO oxidation is one in which the support contributes oxygen through activation of O₂ and a redox cycle similar to a Mars–van Krevelen-type reaction. Although this pathway has been suggested for reducible supports such as Fe₂O₃ and TiO₂ [22], there is little positive evidence for this pathway occurring on oxide-supported Au catalysts.

Non-oxide supports, such as carbides [23,24] and phosphates [25–37], provide additional insight into possible roles of the support in promoting oxygen activation in CO oxidation. Gold nanoparticles can be well dispersed on some metal phosphate supports and show significant activity at rt. Recently, we reported the first observation that the presence of Au species assists the storage of active oxygen species in FePO₄, which opens up two channels for CO oxidation on Au/FePO₄ at rt: Mars–van Krevelen (redox) and direct (e.g. Langmuir–Hinshelwood) mechanisms [28]. To further explore this unexpected result, we have now performed comparative studies between the Au/FePO₄ catalysts and Au supported on a LaPO₄ support that is presumably non-reducible and therefore incapable of a redox pathway. Interestingly, we find that surface hydroxyls on the LaPO₄ open a pathway for CO oxidation in this catalyst system. In the following, we discuss studies of the effects of treatments in oxidizing and reducing environments (both H₂ and CO) and probe their effects upon the support, the Au nanoparticles and the CO oxidation reaction rates.

2. Experimental

2.1. Preparation of Au/LaPO₄ and Au/FePO₄

The LaPO₄ (surface area 56 m²/g) and FePO₄ (surface area 28 m²/g) supports were purchased from Aldrich. Au was emplaced onto LaPO₄ using deposition–precipitation (DP) with a HAuCl₄ precursor. Briefly, 0.6 g HAuCl₄ was dissolved in 100 ml deionized (DI) H₂O, the pH of the solution adjusted to 7 with KOH solution and 2.0 g LaPO₄ was added. The pH value of the solution dropped after adding LaPO₄ and was re-adjusted to approximately 7 by KOH solution. The suspension was stirred at 80 °C for 2 h and then filtered and washed with DI H₂O. The product was dried at 40 °C for two days and stored without further calcination in this “as-synthesized” state. TEM measurements on as-synthesized Au/LaPO₄ showed most Au particles less than 10 nm (Fig. S3a). Au loading was 5.8 wt% as determined by XRF analysis. Au/FePO₄ was synthesized as reported in previous papers, but with a lower Au wt loading of 2.5% as determined by ICP analysis on an IRIS Intrepid II XSP spectrometer (Thermo Electron Corporation). TEM measurements on as-synthesized Au/FePO₄ showed comparable Au particle size as on the Au/LaPO₄ (Fig. S3b).

2.2. Transient FTIR experiments

The chemisorption and reaction experiments were performed using a transient gas switching system for probing catalytic pathways. FTIR spectroscopy was conducted in a diffuse reflectance cell (cell volume about 6 cm³) in a Nicolet Nexus 670 FTIR spectrom-

eter using a MCT/A detector with a spectral resolution of 4 cm⁻¹. After the desired pretreatments, a background spectrum was collected from the sample using 256 scans and 4 cm⁻¹ resolution. Diffuse reflectance FTIR spectra (DRIFTS) were obtained by subtracting the background spectrum from subsequent spectra and are reported herein. Gases leaving the DRIFTS cell were analyzed using a downstream gas sampling quadrupole mass spectrometer (QMS, Pfeiffer–Balzer Omnistar) equipped with a 1 m long gas sampling capillary followed by an apertured entrance into the turbo-pumped QMS chamber.

Prior to data collection, as-synthesized Au/LaPO₄ was pretreated at 200 °C for 2 h in a flowing gas stream of either 2%O₂/He (O₂-pretreated) or 4%H₂/He (H₂-pretreated) and then cooled to rt in He. Then, a selected gas stream was introduced onto the sample with a total flow rate of 15 cm³/min. The gas stream was either pure He, CO (2%CO/2%Ar/He) or a reaction mixture of CO and O₂ at a ratio of 1:4 (2%CO/2%Ar/He mixed with 2%O₂/He). In a typical switching experiment, two gas streams, flowing either through the DRIFTS cell or to a vent, were abruptly interchanged using a 4-way switching valve located upstream from the cell. The times described in the manuscript are relative to the time (*t* = 0) at which the inlet valve was switched. At the flow rate used, a delay time of about 20 s is required to reach the IR cell and about 40 s to reach the QMS. Alternatively, in a typical pulsing experiment, a six-way valve could be used to introduce a 0.5 cm³ gas pulse into one of the gas streams. Both pulsing and switching experiments were carried out.

2.3. CO oxidation and temperature-programmed reduction

CO oxidation activity was tested in a plug-flow, temperature-controlled micro-reactor (Altamira AMI 200). For CO oxidation, the catalyst was loaded into a U-shaped quartz tube (4 mm i.d.) supported by quartz wool. The catalyst was pretreated online in flowing 2%O₂/He at 200 °C for 2 h and then cooled down before switching to the reaction mixture (36 cm³/min mixture of 2%CO/2%Ar/He and 2%O₂/He). A portion of the product gas stream was extracted periodically with an automatic sampling valve and analyzed using a dual-column gas chromatograph with a thermal conductivity detector.

H₂ and CO temperature-programmed reduction (TPR) were also carried out in the AMI 200. Prior to TPR, each sample (50 mg) was first pretreated in 2%O₂/He gas mixture for 2 h at 200 °C. After being cooled down to rt, the sample was purged with high purity He (30 cm³/min) for 15 min. Subsequently, a flow (30 cm³/min) of 4%H₂/He or of 2%CO/2%Ar/He was switched into the system, and the sample was heated under this reducing gas flow from rt to 530 °C at a rate of 10 °C/min. In H₂-TPR, the consumption of H₂ was recorded using a TCD detector located downstream from a cold trap that removed H₂O. The TCD signal was calibrated by integrating pulses of 4%H₂/He from a calibrated loop sent through the TCD. In CO-TPR, the formation of CO₂ (and any H₂) was recorded using a downstream QMS. The QMS was calibrated by integrating pulses of CO₂ from a calibrated loop sent past the QMS sampling port.

3. Results

3.1. Temperature-programmed reduction in H₂

Previous work on Au/FePO₄ catalysts demonstrated that the FePO₄ support undergoes reduction during CO oxidation, contributing structural oxygen to the CO₂ product [28]. Since LaPO₄ is not expected to assume oxidation states lower than La³⁺, it should not be able to contribute oxygen in this way. To verify this expectation, temperature-programmed reduction (TPR) was carried out for

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